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(54) Polymer electrolyte membrane and fuel cell

(57) A polymer electrolyte membrane having outstanding water resistance and high thermal resistance, moreover having practical strength required for use as a polymer electrolyte membrane of a solid polymer electrolyte type fuel cell at low price, and a method for producing the polymer electrolyte membrane are provided. A polymer electrolyte comprising a block copolymer comprising one or more of blocks in which sulfonic acid groups are introduced and one or more blocks in which sulfonic acid groups are not substantially introduced wherein at least one block in the block copolymer is a block having aromatic rings in the polymer chain, and a porous membrane, and a fuel cell using the membrane

are provided.

And moreover the present invention provides a method for producing a polymer electrolyte membrane comprising the steps of, (i) impregnating some of the pores of a porous membrane with a solution (1) of a polymer electrolyte having a contact angle of less than 90° to said porous membrane, (ii) impregnating a remaining part in the pores of the porous membrane with a solution (2) of a polymer electrolyte having a larger contact angle than that of the solution to said porous membrane, and (iii) removing the solvent.

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[0009] However, a problem is brought about if the surface of the porous membrane is hydrophilized by plasma etching because the strength of the porous membrane itself decreases. Besides, in the method of hydrophilizing with a surface active agent or other polymers, a problem occurred that reduction of the amount of polymer electrolyte impregnated in the porous membrane significantly deteriorates the fuel cell characteristics at the time of being used as a polymer electrolyte membrane for solid polymer electrolyte type fuel cells.

[0010] An object of the present invention is to provide a polymer electrolyte membrane having outstanding water resistance and high thermal resistance, moreover having a practical strength required for use as a polymer electrolyte membrane of a solid polymer electrolyte type fuel cell at low price. Furthermore, another object of the present invention is to provide a method for producing a polymer electrolyte composite membrane having good appearance and moreover maintaining original physical properties as porous membrane, without using surface active agent and other polymers.

[0011] These objects could be achieved on the basis of the finding that a composite membrane of a specific polymer electrolyte with a porous membrane demonstrates a practical strength for use as a polymer electrolyte membrane for solid polymer electrolyte type fuel cells, and by providing a method for producing a polymer electrolyte composite membrane having a good appearance and moreover maintaining original physical properties as porous membrane by selecting a solvent having a contact angle to a porous membrane in a specific range as a solvent used for dissolving the polymer electrolyte.

[0012] That is, the present invention provides a polymer electrolyte membrane comprising a porous membrane, and a polymer electrolyte which comprises a block copolymer comprising one or more of blocks in which sulfonic acid groups are introduced and one or more blocks in which sulfonic acid groups are not substantially introduced wherein at least one block in said block copolymer is a block having aromatic rings in the polymer chain of said block polymer; and a fuel cell using the membrane.

[0013] Besides, the present invention provides a method for producing a polymer electrolyte membrane comprising the steps of,

- (i) impregnating pores of a porous membrane with a solution (1) of a polymer electrolyte whose contact angle to the porous membrane is less than 90°;
- (ii) impregnating a remaining part of pores of the porous membrane with a solution (2) of a polymer electrolyte having a larger contact angle than the contact angle of the above described solution (1) to the porous membrane; and
- (iii) removing the solvent.

[0014] In the present invention, a block copolymer is a polymer in which two or more of blocks having different repeating units are bonded directly, or bonded through linkage group, and a block includes two or more repeating units. In the present invention, at least one block is a block having an aromatic ring in the polymer chain.

[0015] In the present invention, a block in which sulfonic acid groups are introduced is a block in which not less than 0.5 sulfonic acid groups (group expressed with $-\text{SO}_3\text{H}$) per one repeating unit on average are bonded to any part of repeating units constituting the block.

[0016] Especially, a block having an aromatic ring, and a block having a structure with sulfonic acid group bonded directly to the aromatic ring is preferable because it may be easily synthesized.

[0017] On the other hand, in the present invention, a block into which sulfonic acid groups are not substantially introduced is a block in which no more than 0.1 sulfonic acid groups per one repeating unit constituting the block on average is introduced.

[0018] A block with aromatic rings introduced in the polymer chain may be a block in which the above described sulfonic acid groups are introduced, or may be a block in which sulfonic acid groups are not substantially introduced, and may be both of the blocks.

[0019] In the present invention as a block in which sulfonic acid groups are introduced, for example, polystyrene, poly(α -methyl styrene), poly(allylphenyl ether), poly(phenyl glycidylether), poly(phenylene ether), poly(phenylene sulfide), poly(ether ether ketone), poly(ether ether sulfone), polysulfone, poly(phenylmethylsiloxane), poly(diphenylsiloxane), poly(phenylmethylphosphazene), poly(diphenylphosphazene), or a block in which sulfonic acid group is introduced into a block comprising a repeating unit having epoxy group are included.

[0020] Among them a block having a repeating unit represented by general formula [1], a block having a repeating unit represented by general formula [2], or a block in which sulfonic acid groups are introduced into a block having epoxy group is preferably used.

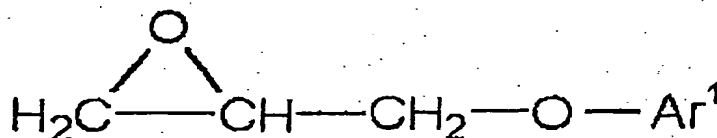
nylene ether), and poly(2,6-diphenyl-1,3-phenylene ether) may be mentioned.

[0022] Among them, poly(1,4-phenylene ether), poly(2-phenyl-1,4-phenylene ether), and poly(2,6-diphenyl-1,4-phenylene ether) are more preferable, and poly(2-phenyl-1,4-phenylene ether) is still more preferable.

[0023] Precursors of a block having repeating units represented by the general formula [1] may be manufactured by well-known methods. For example, a poly(phenylene ether) may be manufactured by an oxidation polymerization method in which phenol is oxidized in the presence of a catalyst, and by a method in which halogenated phenol is condensed in the presence of catalysts and alkalis (called Ullmann reaction).

[0024] A precursor of a block means a polymer having reactive part giving a block copolymer by copolymerization reaction with other polymer having reacting part. (same hereinafter)

[0025] On the other hand, a precursor of a block having repeating units represented by the above described general formula [2], for example, may be obtained by ring opening polymerization of a glycidyl ether having an aromatic ring represented by following formula.



[0026] Specifically phenyl glycidyl ether, o-tolyl glycidyl ether, m-tolyl glycidyl ether, p-tolyl glycidyl ether, 2,3-dimethyl phenyl glycidyl ether, 2,4-dimethyl phenyl glycidyl ether, 2,5-dimethyl phenyl glycidyl ether, 2,6-dimethyl phenyl glycidyl ether, 2,3,4-trimethyl phenyl glycidyl ether, 2,4,6-trimethyl phenyl glycidyl ether, 2,3,4,6-tetramethyl phenyl glycidyl ether, 2-ethyl phenyl glycidyl ether, 4-ethyl phenyl glycidyl ether, 2-propyl phenyl glycidyl ether, 4-n-propyl phenyl glycidyl ether, 4-propyl phenyl glycidyl ether, 2-butyl phenyl glycidyl ether, 4-butyl phenyl glycidyl ether, 4-i-propyl phenyl glycidyl ether, 2-biphenyl glycidyl ether, 4-biphenyl glycidyl ether, 1-naphthyl glycidyl ether and 2-naphthyl glycidyl ether may be mentioned. These may be used independently and may be used as a copolymer using a plurality of glycidyl ethers.

[0027] Besides, it is also possible to use a precursor of a block obtained by copolymerizing glycidyl ethers having the above described aromatic ring, and epoxy compounds not including aromatic ring if needed.

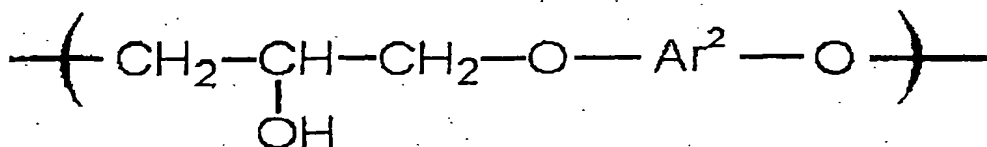
[0028] As epoxy compounds that do not include aromatic ring, for example, ethylene oxide, propylene oxide, 1,2-epoxy butane, cyclohexane epoxide, epifluorohydrin, epichlorohydrin, epibromohydrin, trifluoro propylene oxide, methyl glycidyl ether, ethyl glycidyl ether, propyl glycidyl ether and butyl glycidyl ether may be mentioned.

[0029] When using a polymer or copolymer of above epoxy compound as one component of a precursor of a block, a high ratio of epoxy component may deteriorate the thermal resistance of the resulting block copolymer, and therefore a glycidyl ether component having an aromatic ring is preferably no less than 60 % by weight, and more preferably no less than 80 % by weight.

[0030] As ring opening polymerization of glycidyl ethers having aromatic rings, or of the glycidyl ethers and epoxy compounds not including aromatic rings, many methods are known and each of these well-known polymerization methods may be used. A number of repeating units represented by the general formula [2] is preferably from 2 to 200, and more preferably is from 5 to 50.

[0031] On the other hand, the above-described block having epoxy groups is obtained from a polymer having one or two or more of epoxy groups as a precursor of a block. However, even if a polymer having epoxy groups is not used as a precursor of a block, a block having epoxy groups may include a block in a block copolymer having a epoxy groups as a result.

[0032] In blocks obtained from polymers having epoxy groups, a block comprising polymer having epoxy groups with aromatic rings in the polymer chain is more preferable, and it is still more preferable that it is a block having repeating units represented by general formula [3].



[3]

[0033] In Formula [3], Ar² represents a group selected from following structures.

[0038] In the general formula [4], R^4 represents an alkyl group with carbon numbers of from 1 to 6, and f is an integer of from 0 to 4. When there are two or more R^4 , these may be the same, or may be different from each other. Z represents $-CO-$ or $-SO_2-$.

[0039] Blocks comprising polyether ketones, blocks comprising polyether sulfones may be illustrated.

[0040] Especially polyether sulfones in which Z is $-SO_2-$ in the general formula [4] are preferable because of their high solubility in solvents.

[0041] Polyether sulfones that are examples of a precursor of blocks shown in the general formula [4] may be synthesized by polycondensation of 4,4'-dihydroxy diphenyl sulfone and 4,4'-dichloro diphenyl sulfone.

[0042] The weight-average molecular weight of the precursor of the block obtained from polyether sulfone is preferably from 2000 to 500000, and more preferably from 8000 to 100000. When the molecular weight is smaller than 2000, film strength and thermal resistance of the copolymer may decrease, and when the molecular weight is larger than 500000, solubility may be small.

[0043] A method for producing a polymer electrolyte of the present invention will be hereinafter described.

[0044] There is in particular no limitation in methods for producing block copolymers by chemically bonding precursors of two or more kinds of blocks, and any suitable well-known methods for combining each block may be used.

[0045] For example, in the case where poly(phenylene ether) that is an example of a precursor of a block shown by the general formula [1] as repeating unit, and polyether sulfone that is an example of a precursor of a block shown by the general formula [4] as repeating unit are copolymerized, a method of condensing poly(phenylene ether) having hydroxyl groups remaining at the end of the polymer chain, and polyether sulfone having halogens remaining at the end of the polymer chain under existence of alkali may be illustrated. Besides, when poly(phenylene ether) having hydroxyl groups remaining at the end of the polymer chain, and polyether sulfone having hydroxyl groups remaining at the end of the polymer chain are copolymerized, copolymerization may be conducted by a similar condensation reaction using dihalogenated compounds such as 4,4'-difluoro benzophenone or 4,4'-dichloro diphenyl sulfone as a linking agent for combining poly(phenylene ether) and polyether sulfone to obtain a block copolymer.

[0046] On the other hand, when bonding poly(phenyl glycidyl ether) that is an example of a precursor of a block shown by the general formula [2] as repeating unit, and polyether sulfone that is an example of a precursor of a block shown by the general formula [4] as repeating unit, copolymerization may be conducted by converting end hydroxyl groups, which exist at the end of the polymer chain of polyether sulfone, into metal phenolate, by conducting ring opening polymerization of glycidyl ether including aromatic ring at the alkali metal phenolate as a polymerization starting point, and subsequently by conducting sulfonation.

[0047] Besides, a method may be mentioned in which a precursor of a block is prepared by reacting phenyl glycidyl ether with glycidyl ethers having halogen usable for blocking reaction such as epichlorohydrin, and then the obtained precursor of a block is condensed with polyether sulfones with hydroxyl group remaining at the end of the polymer chain in the presence of alkali.

[0048] Moreover, when polyether sulfone that is an example of a precursor of a block is bonded with an example of a precursor of a block shown by the general formula [3] as a repeating unit, a method may be mentioned in which a hydroxyl group remaining at the end of a polyether sulfone is reacted by a ring opening addition reaction with a glycidyl group remaining at the end of a polymer having epoxy group.

[0049] Although it is possible for block copolymerization to be conducted in a molten state without solvent when using polyether sulfone as one of precursors of a block, it is preferable to conduct the reaction in a suitable solvent. Although as a solvent, aromatic hydrocarbons, ethers, ketones, amides, sulfones, and sulfoxides may be used, amides are preferable because of high solubility of polyether sulfone in amides. As amides, N,N -dimethylformamide, N,N -dimethylacetamide and N -methyl pyrrolidone may be mentioned.

[0050] The reaction temperature of the block copolymerization reaction is preferably 20°C to 250°C , and more preferably it is 50°C to 200°C .

[0051] In a block copolymer used for the present invention, it is preferable that the amount of blocks in which sulfonic acid groups are not substantially introduced is preferably 60 to 95 % by weight of the block copolymer, and more preferably it is 70 to 90 % by weight. When the amount of blocks in which sulfonic acid groups are not substantially introduced is more than 95 % by weight, since sulfonic acid equivalent in the block copolymer is small after introduction of sulfonic acid group, sufficient performance as a polymer electrolyte may not be obtained, and when it is less than 60 % by weight, water resistance of the block copolymer after introduction of sulfonic acid group may be insufficient.

[0052] In a block copolymer used for the present invention, although a method of introducing sulfonic acid groups into a specific block is not limited, the following methods may be illustrated; (a) a method in which a precursor of a block with sulfonic acid groups introduced beforehand and a precursor of a block in which sulfonic acid groups are not substantially introduced are copolymerized, (b) a method in which a copolymer comprising a block in which sulfonic acid groups are to be introduced, and a block in which sulfonic acid groups are not to be substantially introduced is produced, and then sulfonic acid is selectively introduced into the block of this copolymer into which sulfonic acid groups are to be introduced. Regarding the precursor of a block in which sulfonic acid groups are introduced, since

cient, and when it is too large, reinforcement effect to polymer electrolytes may become weak. When the porosity is too small, resistance as a polymer electrolyte membrane will become larger, and when it is too large, generally strength of porous membrane itself will become poor, and reinforcement effect will not be obtained.

[0066] As material of the porous membrane, from viewpoint of thermal resistance and reinforcement effect of physical strength, aliphatic polymers or fluorine polymers are desirable.

[0067] As aliphatic polymers suitably used, polyethylene, polypropylene and ethylene propylene copolymer may be illustrated. Polyethylenes used for the present invention include, for example, copolymers of ethylene and other monomers as well as ethylene homopolymer. Specifically, copolymers of ethylene and α -olefins referred to as linear low density polyethylene (LLDPE) are included. Besides, polypropylenes include, for example, propylene block copolymers and random copolymers (these are copolymers with e.g. ethylene and 1-butene).

[0068] Besides, as fluorinated polymers, well-known thermoplastic resins having at least one carbon-fluorine bond in the molecule may be used without any limitation. Usually, resins having a structure where all or most of the hydrogens of aliphatic polymers are substituted by fluorine atoms are suitably used.

[0069] Fluorinated resins, for example, may be poly(trifluoroethylene), poly(tetrafluoroethylene), poly(chloro trifluoroethylene), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoro alkylether) and poly(vinylidene fluoride), but the present invention is not limited by them. Among them, in the present invention, poly(tetrafluoroethylene) and poly(tetrafluoroethylene-hexafluoropropylene) are preferable, and poly(tetrafluoroethylene) is more preferable. From viewpoint of excellent mechanical strength, fluorinated resins having an average molecular weight of not less than 100000 are preferable.

[0070] A polymer electrolyte membrane of the present invention is a polymer electrolyte membrane in which the above described polymer electrolyte and the above described porous membrane are combined. As combining methods, for example; a method in which a porous membrane is impregnated with a polymer electrolyte solution, the porous membrane is taken out, and then the solvent is evaporated to obtain a composite membrane; a method in which a polymer electrolyte solution is applied to a porous membrane, and then the solvent is evaporated to obtain a composite membrane; and a method in which a polymer electrolyte solution is contacted to a porous membrane under reduced pressure, then the pressure is returned to ordinary pressure to impregnate the solution into the porous membrane pores, and subsequently the solvent is evaporated to obtain a composite membrane may be illustrated. Above all, since a polymer electrolyte composite membrane having good appearance and maintaining physical properties of an original porous membrane may be produced, a method comprising,

(i) a step in which pores of a porous membrane are impregnated with a solution (1) of a polymer electrolyte having a contact angle of less than 90° to the porous membrane,

(ii) a step in which a remaining part of pores of the porous membrane is impregnated with a solution (2) of a polymer electrolyte having a larger contact angle than the contact angle of the above described solution (1) to the porous membrane, and

(iii) a step in which the solvent is removed, is desirable.

[0071] As the filling method of a polymer electrolyte, a method is adopted in which after a solution of a polymer electrolyte dissolved in a solvent is impregnated into a porous membrane, the solvent is removed. As methods of impregnating, a method in which the solution is applied or sprayed to the porous membrane may be adopted, or a method in which the porous membrane is immersed in the solution may be adopted. Besides, any of methods such as heating, reducing pressure, air-drying, and combination of these may be used as methods of removing solvent.

[0072] A solvent of the polymer electrolyte solution (1) in step (i) will not be limited in particular, if it is a solvent in which a contact angle of the polymer electrolyte solution (1) to the porous membrane gives less than 90° when the electrolyte is dissolved. As these solvents, for example, solvents containing chlorine, such as dichloromethane, chloroform, 1,2-dichloroethane, chlorobenzene, and dichlorobenzene; alcohols, such as methanol, ethanol, and propanol; and mixtures of two or more kinds of these solvents may be used.

[0073] Moreover, filling of an electrolyte in this step is conducted so that part of the pores of the porous membrane may remain not filled with an electrolyte. The amount of filling is usually less than 80% in volume of the pores, preferably less than 60%, and more preferably less than 40%. When too large degree of filling is conducted in this step, filling in the following step will become difficult.

[0074] As solvent of solution (2) of polymer electrolyte in step of (ii), when an electrolyte is dissolved, a solvent giving a larger contact angle of a solution (2) of polyelectrolyte to the porous membrane than the contact angle of a solution (1) of polyelectrolyte used in step (i) is used. More preferably, a solvent giving a contact angle of not less than 90° to a porous membrane of solution (2) of polymer electrolyte is preferable.

[0075] Moreover, if water still remains in a combined membrane after removing the solvent, a combined membrane with poor appearance may be obtained, because the combined membrane have bubbles, unevenness and low strength. Therefore when a solvent which easily absorbs water in air is used, a boiling point of the solvent is preferably no less

Measurement of the amount of impregnated polymer electrolyte in a porous membrane

[0088] A section of a composite membrane of a porous membrane and a polymer electrolyte membrane was observed using FE-SEM S900 Hitachi LTD., and FE-SEM-EDX analysis (field emission type scanning electron microscope-energy dispersion X ray analysis) was conducted for sulfur atoms in the section. The number of sulfur atoms was counted in a portion of polymer electrolyte layers on both surfaces of the composite membrane and in a portion where polymer electrolyte was combined with the porous membrane. When the number of counts of sulfur atoms was corrected in consideration of porosity of the porous membrane, and both of the counts were almost the same, it was judged that the polymer electrolyte was filled in the pores.

Measurement of water absorption

[0089] The polymer electrolyte membrane was dipped into ion-exchanged water, and was boiled at 100°C for 2 hours, and subsequently the polymer electrolyte membrane was removed from the water. After surface water was wiped off, water absorption was measured according to the following equation using HR73 type halogen aquameter (Halogen Moisture Analyzer, manufactured by METTLER TOLEDO).

$$(\text{Moisture content}) = 100 \times ((\text{weight of film with water absorbed}) - (\text{weight of dried film})) / (\text{weight of dried film})$$

Evaluation of Fuel cell characterization

[0090] Platinum catalyst carried on fibrous carbon and porous carbon woven fabrics as current collector were joined to both sides of a polymer electrolyte membrane. Humidified oxygen gas was supplied to one side of this unit, and humidified hydrogen gas to another side to evaluate power generation characteristics of this joined body.

Manufacturing Example 1

Manufacturing example of polymer electrolyte (P1)

[0091] 99 mg anhydrous cuprous chloride and 266 mg 2-methyl benzoxazole were stirred in 1 ml toluene at room temperature under atmospheric condition for 15 minutes. 8.5 g 2-phenylphenol and 30 ml toluene were added to the mixture, and stirred at 50°C under oxygen atmosphere for five hours. Resulting mixture was poured into methanol including hydrochloric acid after completion of reaction, and a polymer was precipitated. The polymer was filtered and dried to obtain poly(2-phenylphenylene ether) (referred to as PE1, hereinafter).

[0092] To a flask equipped with azeotropic distillation equipment 3.0 g Sumika Excel PES5003P (polyether sulfone with hydroxyl end groups, manufactured by Sumitomo Chemical Co., Ltd.), 0.75 g PE1, 0.04 g potassium carbonate, 15 ml N,N-dimethylacetamide (referred to as DMAc hereinafter) and 3 ml toluene were added. Mixture obtained was heated and agitated, and after water was removed off under azeotropic condition of toluene and water, toluene was distilled off. 0.05 g 4,4'-difluorobenzophenone was added, and heating and agitation were carried out at 160°C for five hours. Reaction liquid obtained was pored into a large quantity of acidic methanol with hydrochloric acid, obtained precipitate was recovered by filtration, and dried under reduced pressure at 80°C to obtain 3.8 g block copolymer.

[0093] 2 g of the obtained block copolymer was stirred at room temperature with 20 ml of 98% sulfuric acid to obtain a uniform solution, and subsequently stirring was continued for further two hours. Obtained solution was pored into a large quantity of iced water, and obtained precipitate was recovered by filtration. Washing by mixer with ion-exchanged water was further repeated until washing liquid showed neutral, and drying at 40°C under reduced pressure was given to obtain a sulfonated block copolymer. Hereinafter, the polymer electrolyte may be referred to as (P1).

Manufacturing example 2

Manufacturing example of polymer electrolyte (P2)

[0094] Using same catalyst as manufacturing example 1, using chlorobenzene as solvent, oxidation polymerization of 12.25 g 2-phenylphenol and 1.49 g 4,4'-dihydroxy biphenyl as monomers was carried out to obtain poly(2-phenylphenylene ether) (referred to as PE2 hereinafter) having hydroxyl groups at both ends.

[0095] Into a flask equipped with azeotropic distillation equipment, 50 g Sumika Excel PES5003P, 0.36 g potassium carbonate, 180 ml DMAc, and 25 ml toluene were added. Under nitrogen, and after heating and stirring were continued for two hours and water was removed under azeotropic condition of toluene and water, toluene was evaporated off.

polytetrafluoroethylene porous membrane.

[0105] P1 was dissolved in a methanol / dichloromethane mixed solvent at a concentration of 15 % by mass, and the solution was applied on a polytetrafluoroethylene porous membrane (15 μm of membrane thickness, 90% of porosity, 3.0 μm of pore size) currently fixed on a glass plate. Solvent was dried under ordinary pressure and a target polymer electrolyte membrane was obtained.

Examples 3 and 4

[0106] Manufacture of a polymer electrolyte membrane obtained by combining the polymer electrolyte (P2) or (P3) and a polytetrafluoroethylene porous membrane.

[0107] By a same procedure as in Example 2, a polymer electrolyte membrane obtained by combining the polymer electrolyte (P2) and a polytetrafluoroethylene porous membrane, or a polymer electrolyte membrane obtained by combining the (P3) and a polytetrafluoroethylene porous membrane were prepared.

Comparative example 1

Manufacture of membrane comprising the polymer electrolyte (P1).

[0108] P1 was dissolved in DMAc at a concentration of 15 % by mass, and it was flowed wide spread on a glass plate. Solvent was dried under ordinary pressure and a target polymer electrolyte membrane was obtained.

Comparative examples 2 and 3

Manufacture of membranes comprising polymer electrolyte (P2) or (P3).

[0109] By a same procedure as in comparative example 1, the polymer electrolyte P2 or P3 was dissolved in DMAc at a concentration of 15 % by mass, and it was flowed wide spread on a glass plate. Solvent was dried under ordinary pressure and a target polymer electrolyte membrane was obtained.

[0110] Polymer electrolyte membranes obtained in examples 1 to 4 and comparative examples 1 to 3 were measured for proton conductivity and water absorption. Results are summarized in following Table 1.

Table 1

	Polymer electrolyte	Porous membrane material	Proton conductivity (S/cm)	Water absorption (%)
Example 1	P1	Polyethylene	4.7×10^{-2}	38
Example 2	P1	Polytetrafluoroethylene	8.5×10^{-2}	60
Comparative example 1	P1	Not used	1.0×10^{-1}	79
Example 3	P2	Polytetrafluoroethylene	7.2×10^{-2}	49
Comparative example 2	P2	Not used	8.4×10^{-2}	63
Example 4	P3	Polytetrafluoroethylene	4.3×10^{-2}	30
Comparative example 3	P3	Not used	5.1×10^{-2}	38

[0111] Polymer electrolyte membranes obtained in examples 1 to 4 were evaluated for fuel cell characteristics. Cycles of operation and stop operation was repeated and evaluation was continued for one week. As a result, neither deterioration of fuel cell characteristic, nor gas leak were observed.

[0112] On the other hand, when polymer electrolyte membranes obtained in comparative examples 1 to 3 were evaluated for same fuel cell characteristics, and after one week, gas leak was observed in all cases, and deterioration of characteristics was also observed.

[Table 2] (continued)

	Appearance of composite membrane	Proton conductivity (S/cm)
	○: no unevenness and bubble not observed	
	×: unevenness and bubble observed.	

[0118] The amount of filling of polymer electrolytes in porous membranes was measured for Example 5 and Comparative example 4. Results are shown in Table 3.

[Table 3]

EDX analysis (number of counts of sulfur atom)		
	Portion obtained only by polymer electrolyte membrane	Portion where a polymer electrolyte is complexed
Example 5	1500	1300
Comparative example 4	2700	250

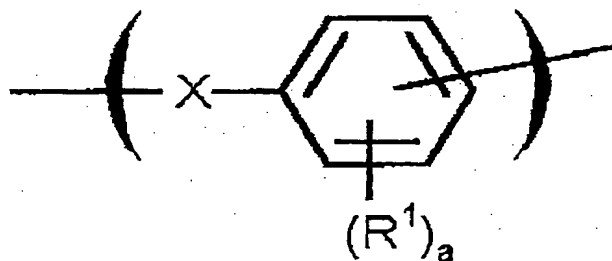
[0119] Composite membranes of Example 5 and Comparative example 5, and electrolyte membrane of comparative example 6 were evaluated for fuel cell characteristics. Cycles of operation and stop operation were repeated. Results after one week are shown in Table 4.

[Table 4]

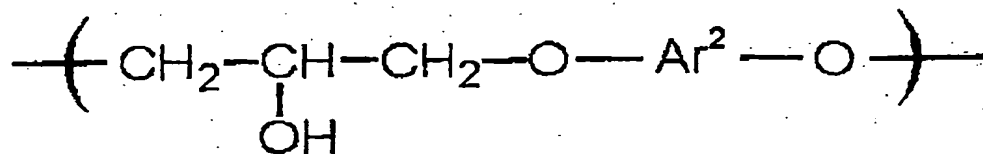
Fuel cell characteristics	
Example 5	Neither deterioration of characteristics nor gas leak were observed.
Comparative example 5	Gas leak occurred and deterioration of characteristics was observed.
Comparative example 6	Gas leak occurred and deterioration of characteristics was observed.

Claims

1. A polymer electrolyte membrane comprising a polymer electrolyte comprising;
a block copolymer comprising one or more blocks in which sulfonic acid groups are introduced and one or more blocks in which sulfonic acid groups are not substantially introduced, wherein at least one block in said block copolymer is a block having aromatic rings in the polymer chain, and
a porous membrane.
2. The polymer electrolyte membrane according to claim 1, wherein a block in which sulfonic acid groups are introduced is a block that has a structure having sulfonic acid groups on aromatic rings.
3. The polymer electrolyte membrane according to claim 1, wherein a block in which sulfonic acid groups are introduced is a block in which sulfonic acid groups are introduced into a block having repeating units represented by general formula [1].

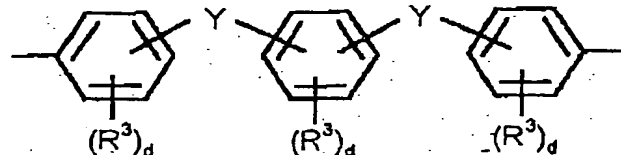
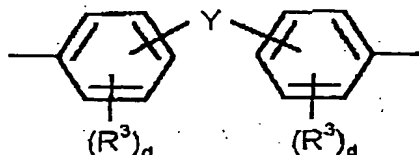
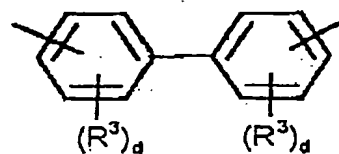
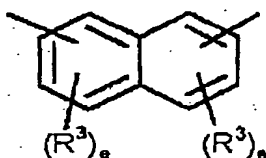
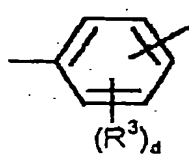


[1]



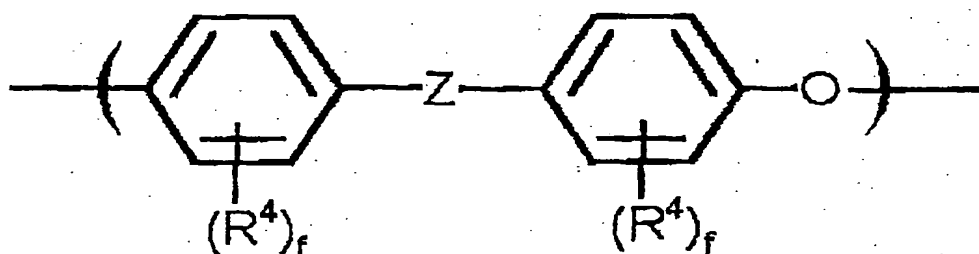
[3]

(In formula [3], Ar^2 represents a group selected from following structures.)



(In the above described formulas, R^3 represents an alkyl group with carbon numbers of from 1 to 6, alkoxy group with carbon numbers of from 1 to 6, or phenyl group, d is an integer of from 0 to 3, and e is an integer of from 0 to 2. When there are two or more R^3 , these may be the same, or may be different from each other. Y represents $-\text{O}-$, $-\text{S}-$, an alkylene group with carbon numbers of from 1 to 20, halogenated alkylene group with carbon numbers of from 1 to 10, or alkylendioxy group with carbon numbers of from 1 to 20. When there are two or more Y , these may be the same or different from each other.)

8. The polymer electrolyte membrane according to claim 1, wherein a block in which sulfonic acid groups are not substantially introduced is an aromatic polyether having repeating units represented by general formula [4].



[4]

(In the formula [4], R^4 represents an alkyl group with carbon numbers of from 1 to 6, and f is an integer of from 0 to 4. When there are two or more R^4 , these may be the same or different from each other. Z represents $-\text{CO}-$ or $-\text{SO}_2-$.)

9. The polymer electrolyte membrane according to claim 8, wherein Z is $-\text{SO}_2-$ in the general formula [4].
10. The polymer electrolyte membrane according to claims 1 to 9, wherein a block in which sulfonic acid groups are not substantially introduced is from 60 to 95 % by weight of block copolymer.

